Electronic Supplementary Material (ESI) for Dalton Transactions.

Remarkable Structural Effects on the Complexation of Actinides with H-Phosphonates: A Combined Experimental and Quantum Chemical Study

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Supporting Information

Experimental

Materials and instruments

Phosphorus trichloride (Fluka), 1-butanol, *iso*–butanol, *sec*–butanol (Merck), toluene and *n*–dodecane were obtained from Lancaster. ^{233}U was purified by extraction in the form of uranyl nitrate from 4M nitric acid with 5% TBP/*n*– dodecane; this was followed by scrubbing with 4M nitric acid and stripping with dilute nitric acid. This procedure was adopted for separation of ^{233}U from impurities and was used as tracer for uranium extraction studies. Am(III) solution was prepared by dissolving Am_2O_3 in concentrated HNO_3 (~16N) and diluting to the desired concentration.

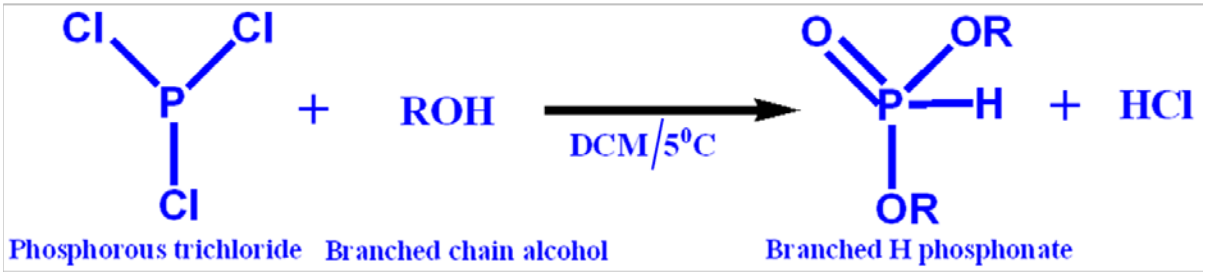
^{1}H and ^{31}P [^{1}H]–NMR spectra were recorded by BRUKER DMX–400 and all ^{1}H chemical shifts were reported relative to the residual proton resonance in deuterated solvents (all at 25°C, $CDCl_3$). H_3PO_4 was used as an external standard for ^{31}P [^{1}H]–NMR.

The H–phosphonates were analysed for their molecular weight using a Perkin Elmer GC-MS instrument. Infrared spectra of the samples were recorded in the range 4000 to 500 cm^{-1}, using a Vertex 70 FTIR spectrometer, operated at a resolution of 0.5 cm^{-1} using liquid N_2 cooled mercury cadmium telluride (MCT) detector.

ESI MS analysis was carried out using an Applied Biosystems 3200 QTRAP LC/MS/MS system in the mass range of m/z 80 to 1700. Optimized conditions were as follows: Ion spray Voltage 3.2 kV; Declustering Potential (DP) 50 V, Entrance Potential (EP) 10 V.

General procedure for the synthesis of H–phosphonates

One equivalent of phosphorous trichloride was dissolved in twice the volume of dichloromethane and stirred in a round bottom flask kept in an ice bath. Three equivalents of the appropriate alcohol (eg. 1 – butanol, iso – butanol, sec – butanol) diluted in two volumes of dichloromethane were added drop–wise to the cooled reaction flask. Once addition was complete, the reaction was stirred overnight and then quenched with an ice water mixture. Hydrochloric acid was a by–product, which was removed by washing with sodium carbonate until the wash water was basic. The aqueous and organic phases were subsequently separated using a separating funnel and the organic phase was thoroughly washed with water to remove excess carbonate and any other water soluble impurities. Sodium sulphate was added to the separated organic phase and left to stand in order to remove any moisture present in the organic phase. Finally the organic phase containing the product was placed in a rotary evaporator for three hours to remove the volatile solvent (dichloromethane) and other impurities. The reaction scheme is represented in Scheme 1.



Scheme 1: Preparation route for H–phosphonates from the starting materials phosphorous trichloride and branched alcohol.

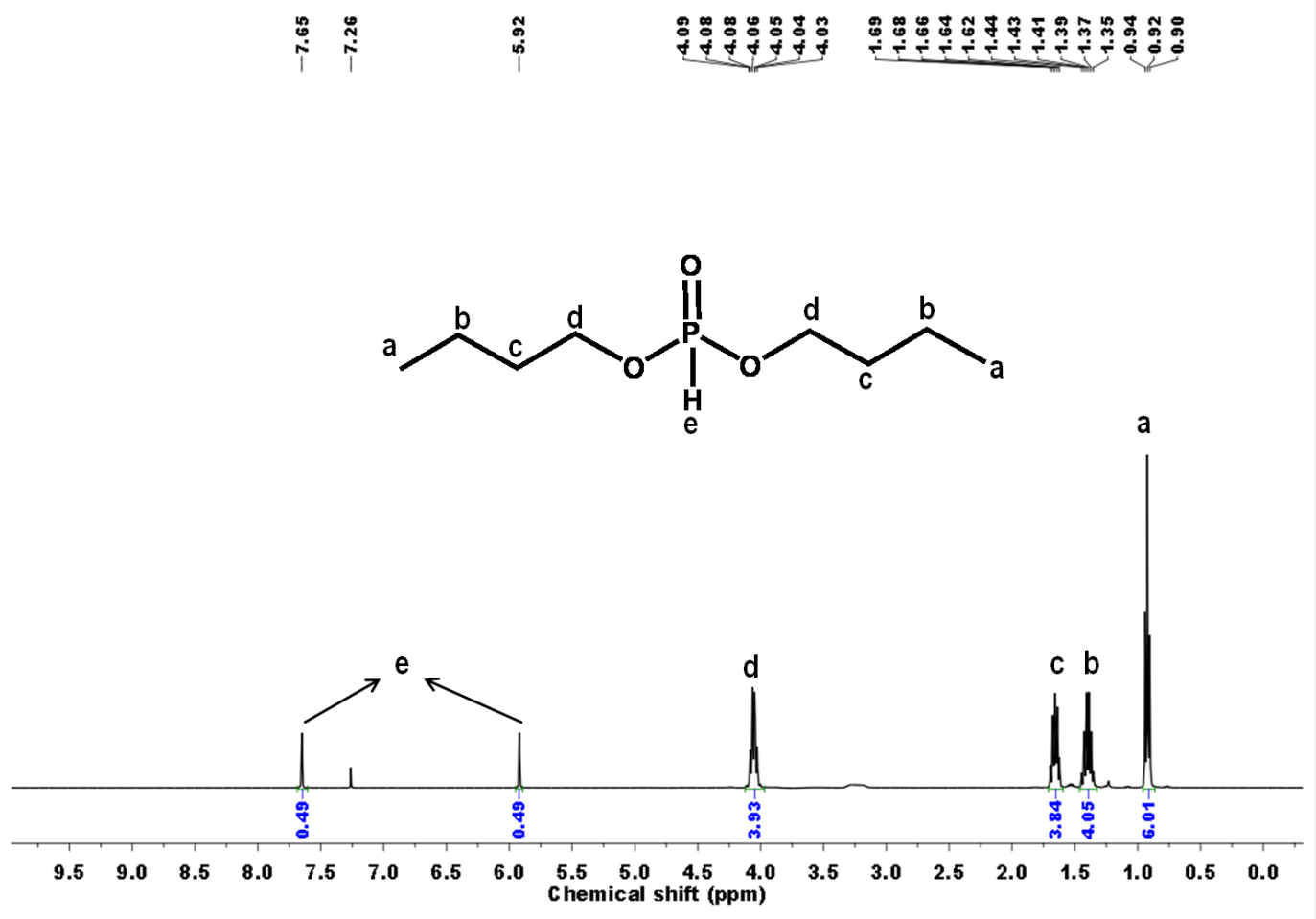


Figure 1S: Proton NMR spectrum of Dibutyl H phosphonate (DBHP)

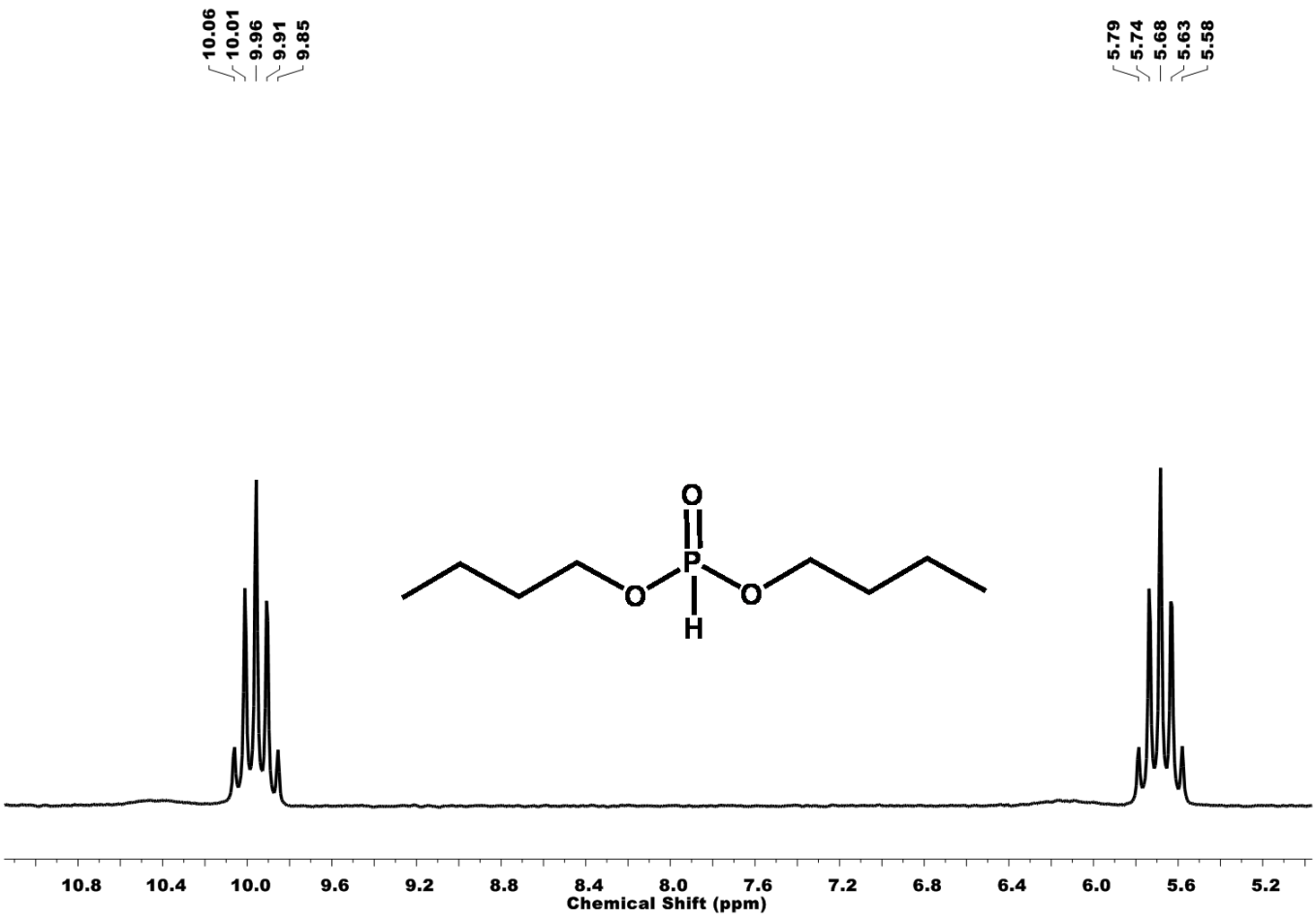


Figure 2S: ^{31}P NMR spectrum of Dibutyl H phosphonate (DBHP).

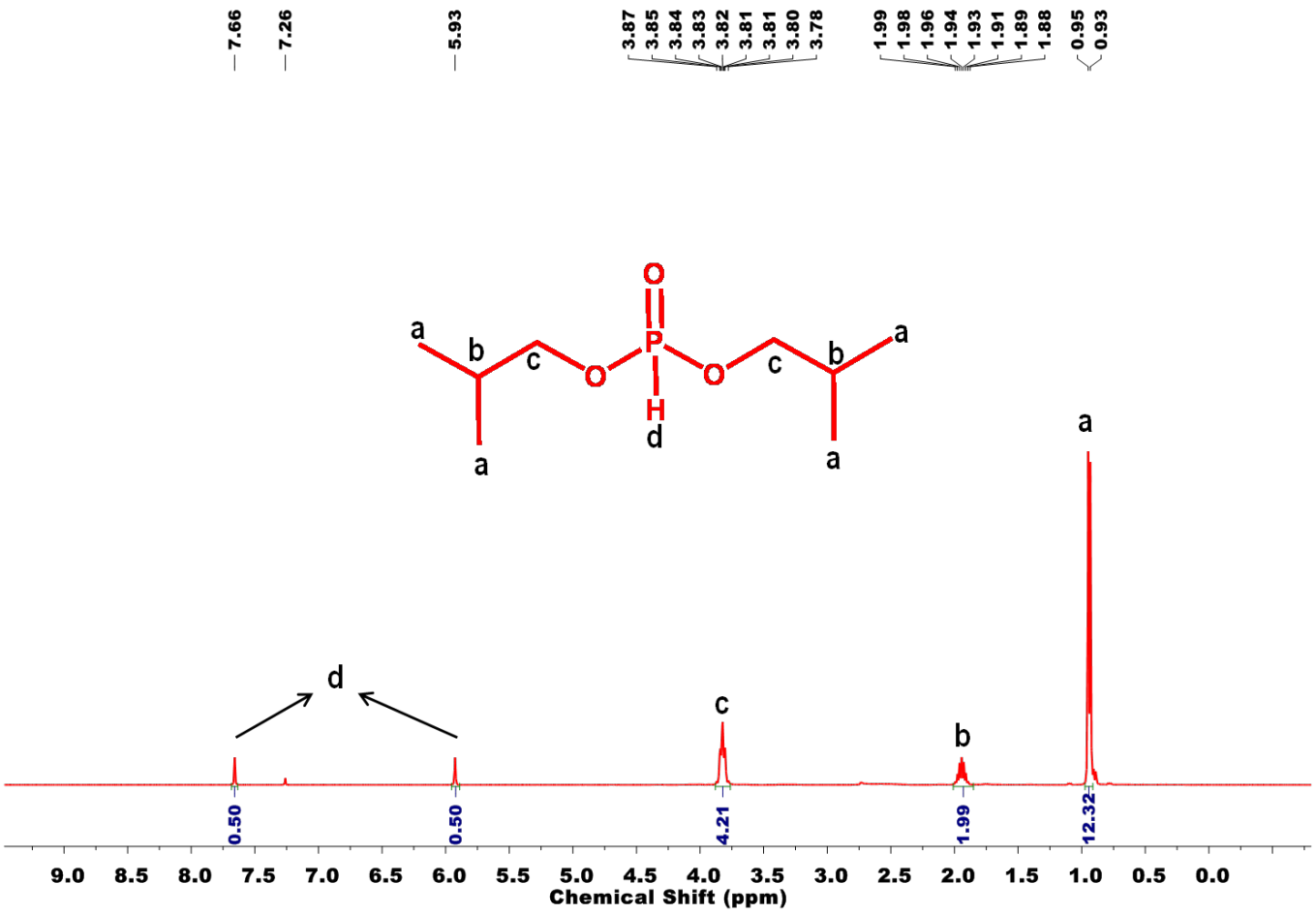


Figure 3S: Proton NMR spectrum of Diisobutyl H phosphonate (DiBHP)

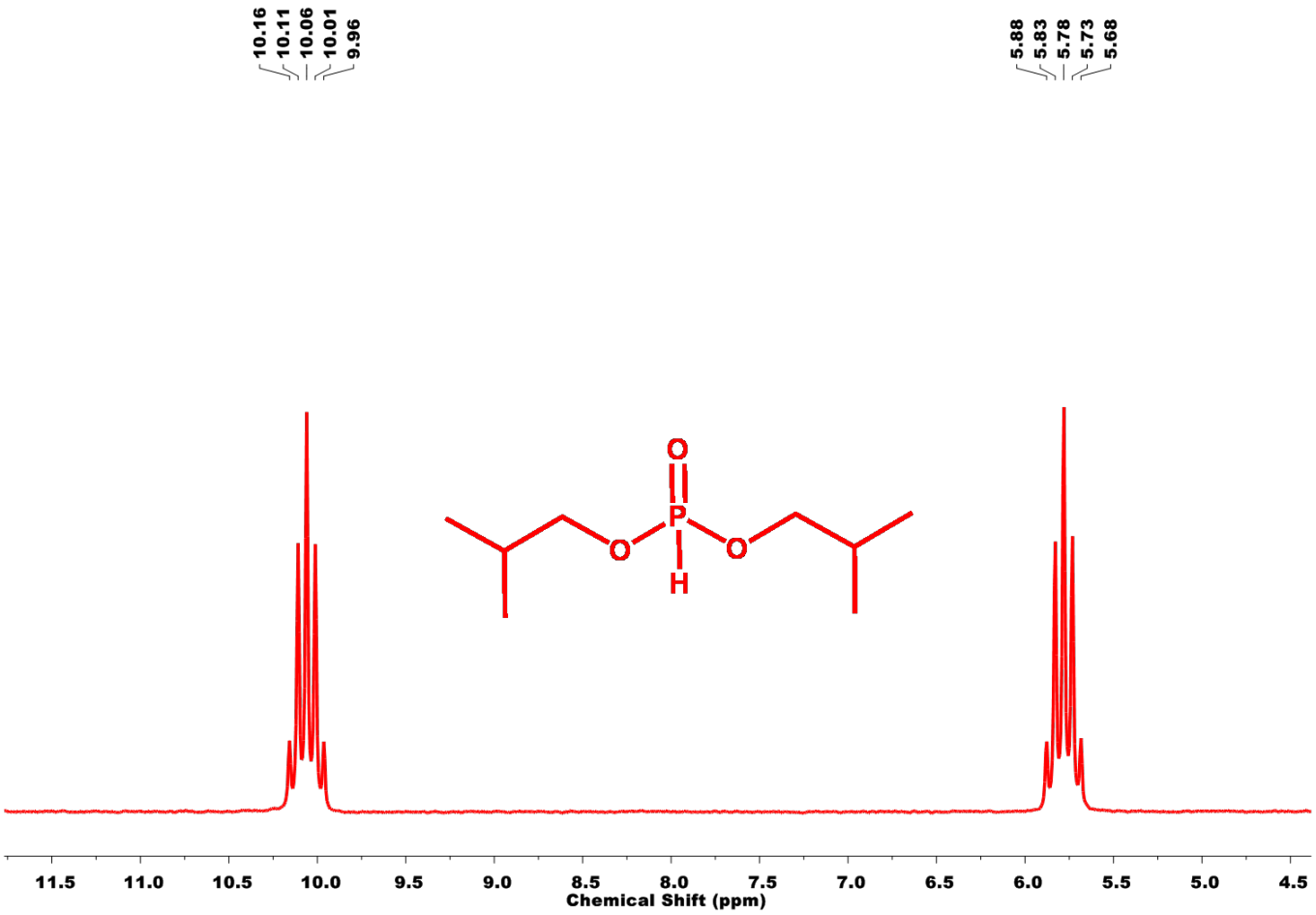


Figure 4S: ^{31}P NMR spectrum of Diisobutyl H phosphonate (DiBHP).

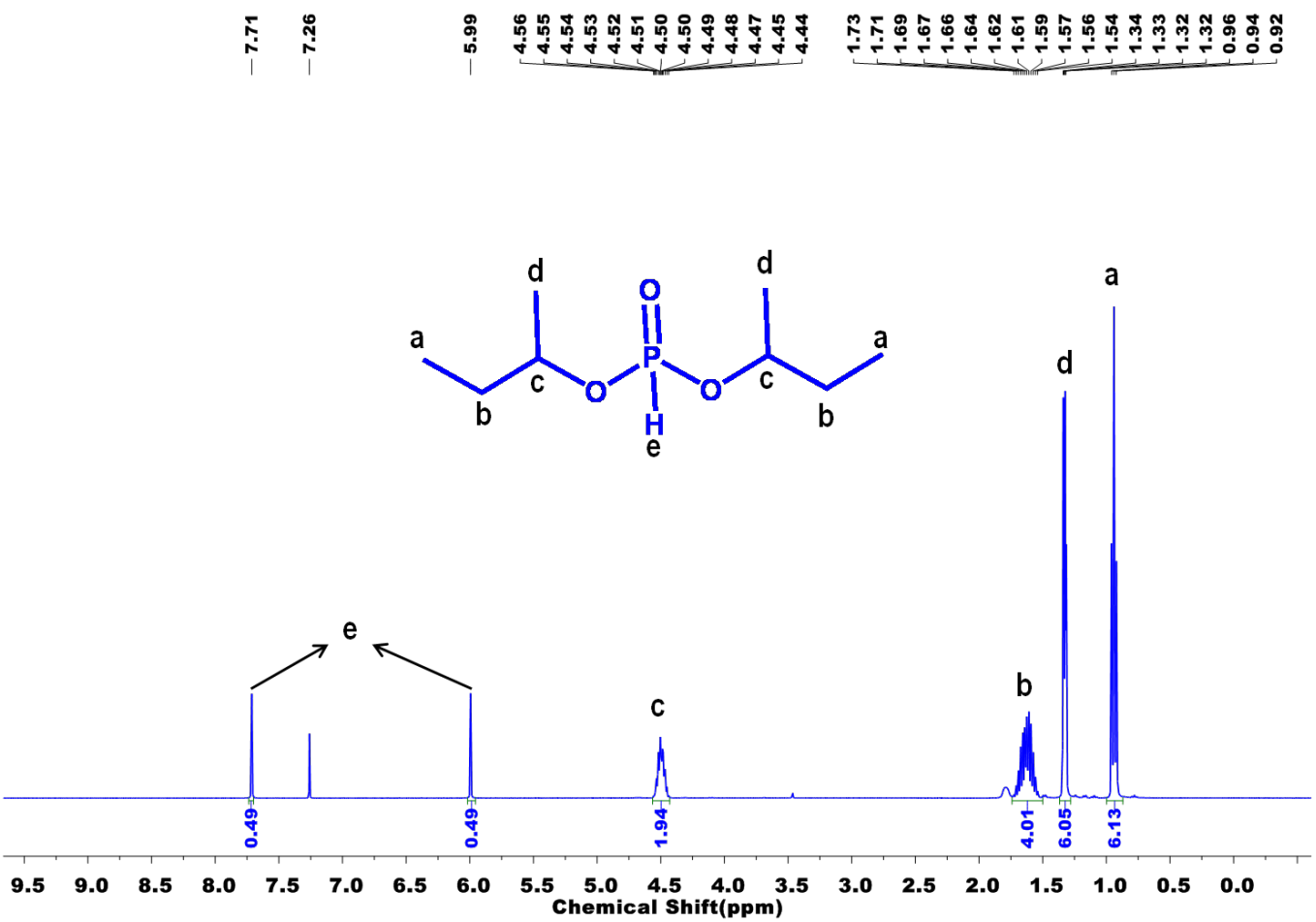


Figure 5S: Proton NMR spectrum of Disecbutyl H phosphonate (DsBHP)

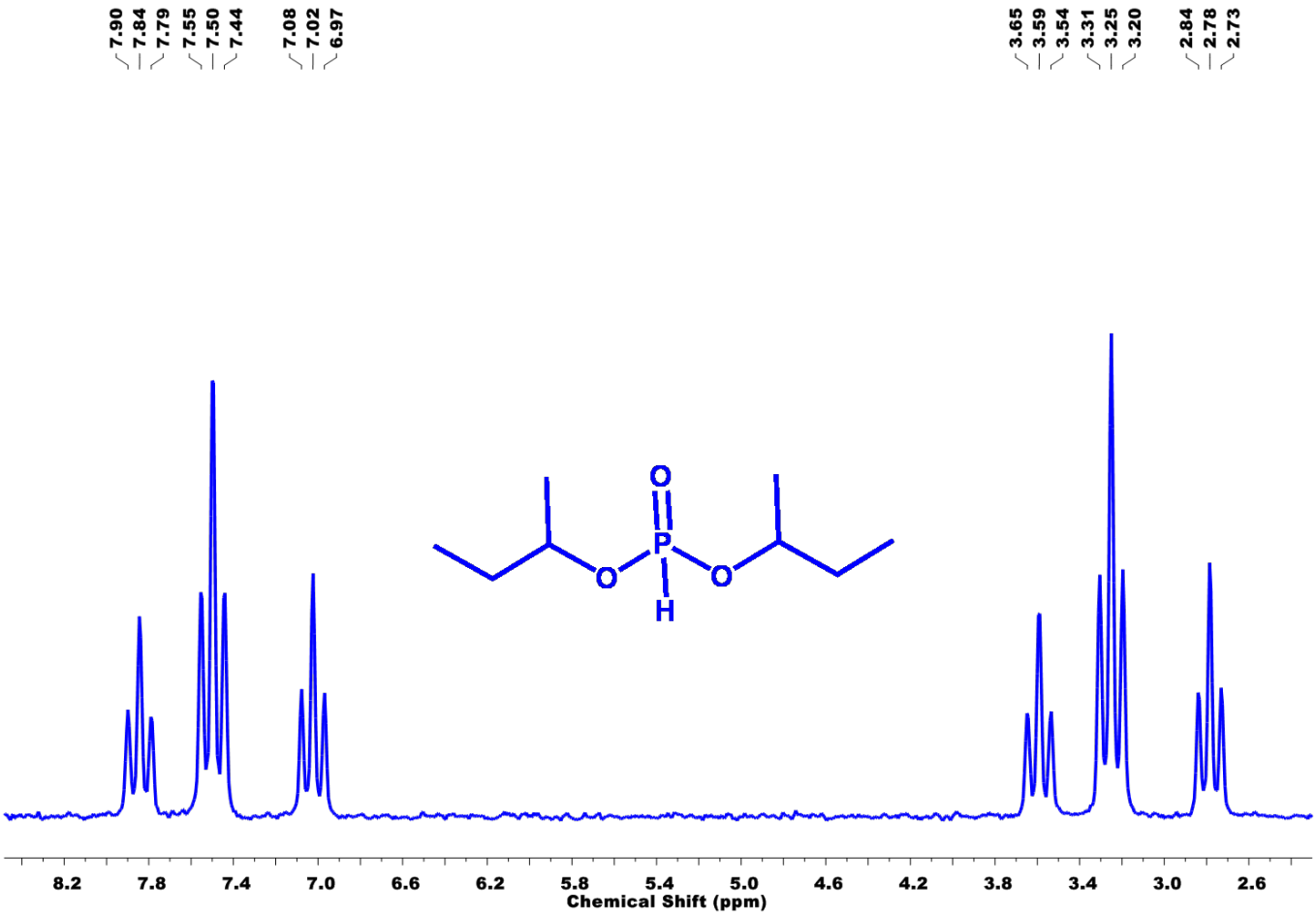


Figure 6S: ^{31}P NMR spectrum of Disecbutyl H phosphonate (DsBHP).

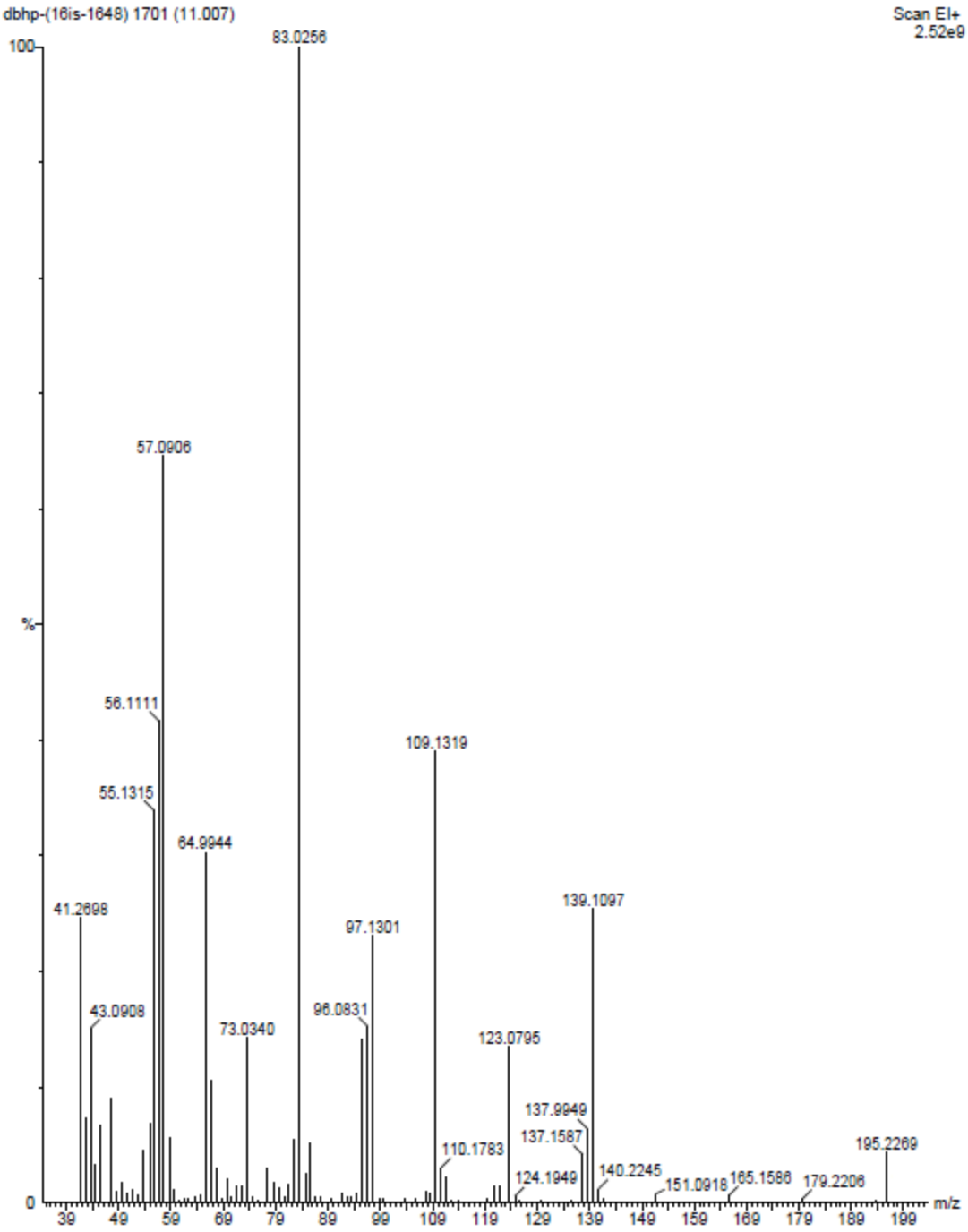


Figure 7S: GC – MS spectrum for DBHP

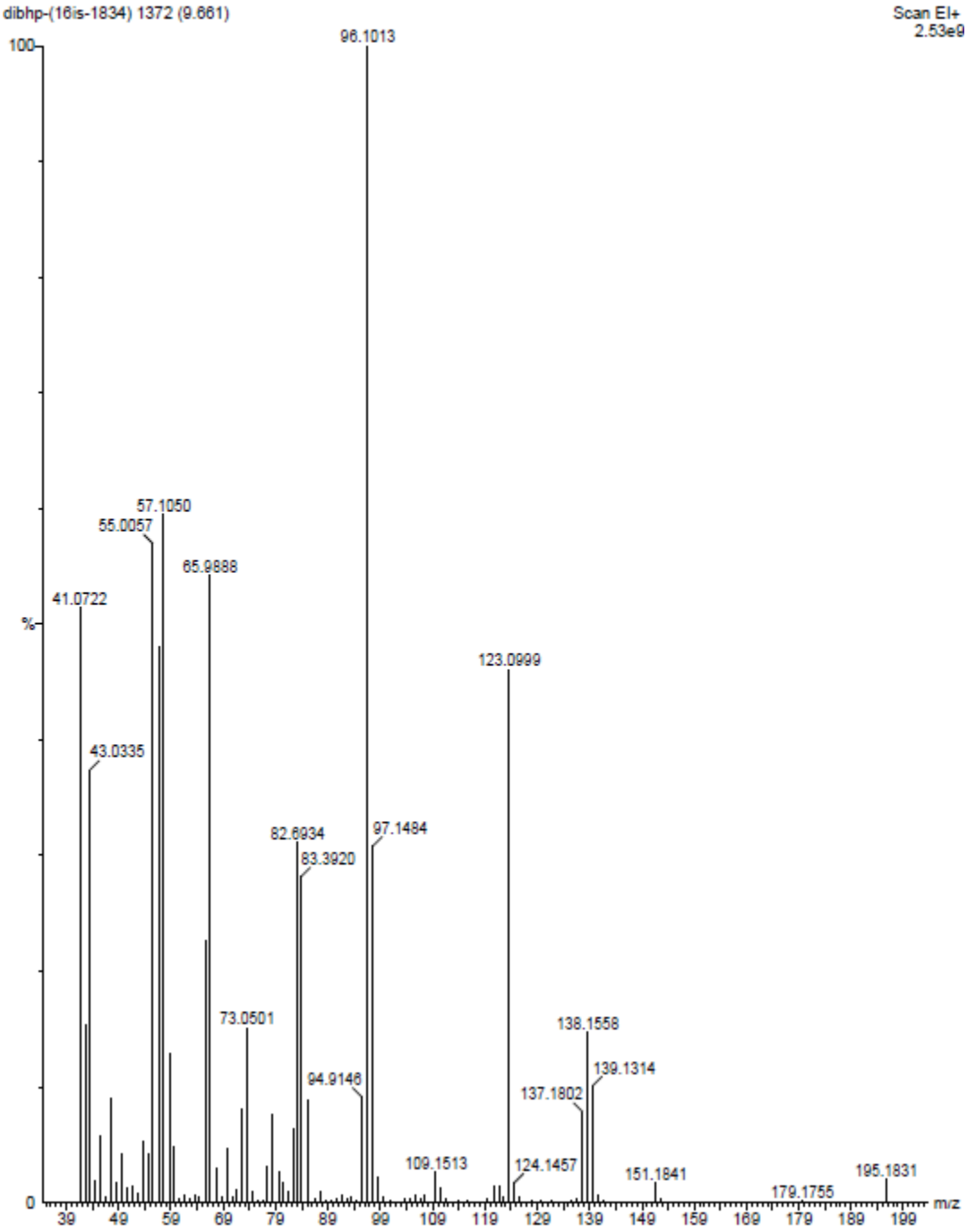


Figure 8S: GC – MS spectrum for DiBHP

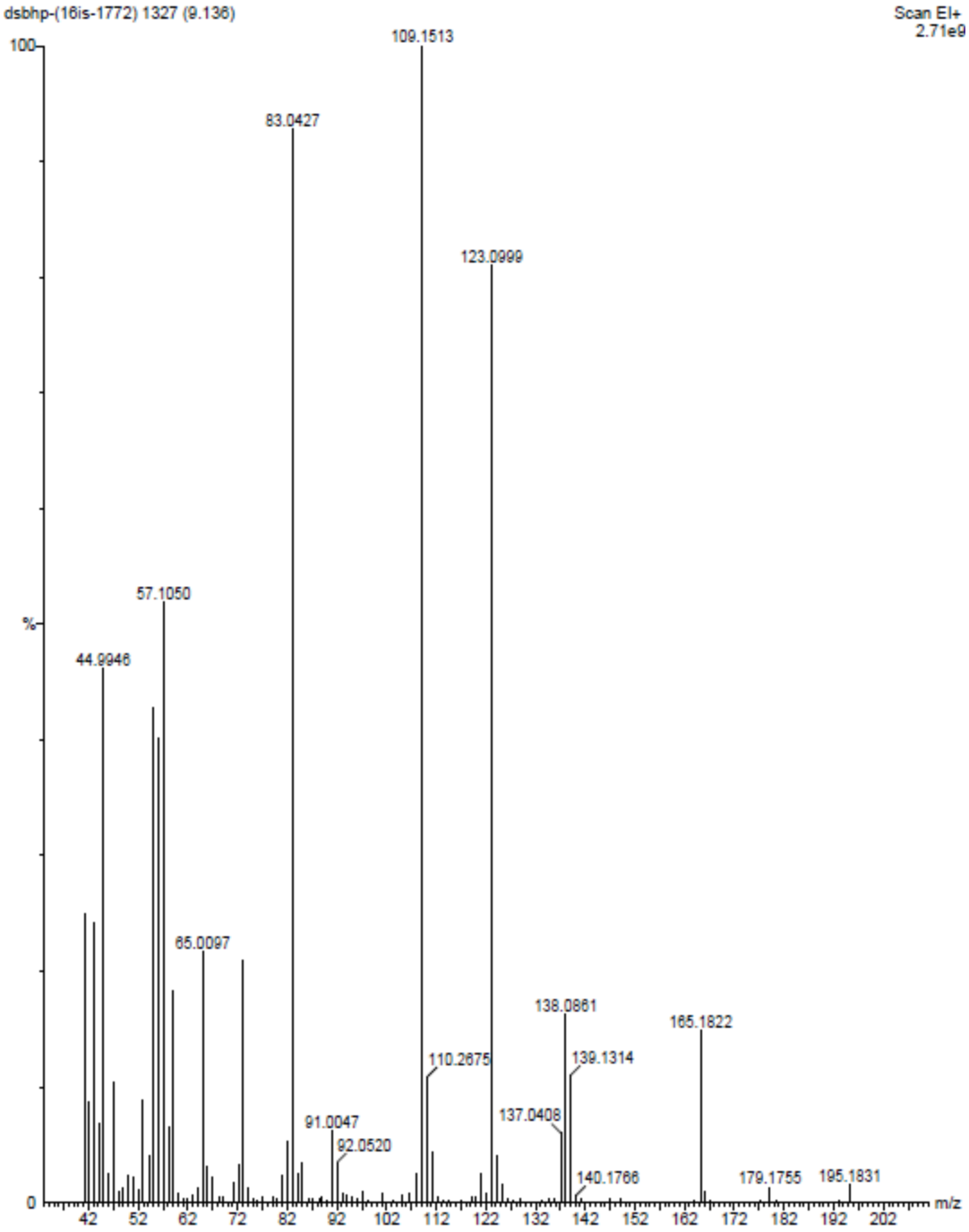


Figure 9S: GC – MS spectrum for DsBHP

Physicochemical properties of H–phosphonates

Measurement of density

Density is an important parameter for a system to qualify as a suitable extractant for the solvent extraction process. The density difference between the aqueous and organic phase must be large enough in order to minimise phase separation time. Density of the synthesised extractants was measured using a 500µL glass pipette. The density was calculated from the weight difference of the pipette before and after it was filled with the compound.

Measurement of viscosity

Viscosity of an extractant influences mass transfer between phases. It plays a vital role in predicting the nature of flow in any process. Measuring viscosity is useful in the calculation of the power requirements for the unit operations such as mixing, pipeline design and pump characteristics. Viscosity of a fluid can be determined by measuring the time of flow of a given volume of liquid through a vertical capillary under the influence of gravity:

$$\eta = \frac{\pi \Delta p t r^4}{8 l V}$$

Where η is the viscosity of the fluid, Δp is the difference in the pressure between two ends of the tube, t is the time for volume V to flow out, r is the radius of the capillary and l is the length of the capillary (31). With both ends of the viscometer tube open:

$$\eta = \frac{\pi h \rho g t r^4}{8 l V}$$

Where h is difference in height between the liquid levels in the two reservoirs used in the experiment, ρ is density of the liquid and g is acceleration due to gravity. For a given volume of liquid and a given viscometer

$$\eta = k\rho t$$

Where $k = \frac{\pi h g r^4}{8lV}$

Additionally viscosity is related to the activation energy of liquid flow E_a, by the equation

$$\eta = Ae^{\frac{E_a}{RT}}$$

Where A is a constant, T is the temperature and R is the gas constant.

The viscosity of the extractants (DBHP, DiBHP and DsBHP) was measured by Oswald viscometer (32). A known volume (~ 15mL) of liquid was taken in the viscometer and the time taken by the liquid to flow through the marked region of the Oswald viscometer was measured. The driving pressure p at all stages of the flow of a liquid is given by $h\rho g$, where h is the difference in the heights of the liquid in upper and lower bulb, ρ the density of the liquid and g the acceleration due to gravity. The viscosity of fluids can be evaluated by the comparative method where one of the fluids is water whose density and viscosity as a function of temperature are well reported in the literature. The viscosity of the fluid of interest can be determined using the following expression.

$$\frac{\eta_e}{\eta_w} = \frac{\rho_e t_e}{\rho_w t_w}$$

Where η_e, $\rho_e$and t_e are the viscosity, density and time taken for the extractant to pass through the marked region of the viscometer of the fluid to be determined. η_w, $\rho_w$and t_w are the viscosity, the density and the time for the water system under identical conditions. Viscosity measurements were carried out for DBHP, DiBHP and DsBHP and the natural logarithm of viscosity was plotted against the inverse of temperature. Linear plots were obtained and from the slope of the graphs, activation energy was calculated as the slope of the graphs give *Ea/R.*

Measurement of aqueous solubility

An equal volume of extractant and distilled water were equilibrated in a glass equilibration tube for 8 hours. The two phases were transferred to a separating funnel and allowed to settle for 24 h. Once the phase separation was complete, the aqueous layer was carefully separated using a pipette and analysed for the total carbon content using Total Organic Carbon (TOC) analyser. The solubilities of the H–phosphonates were determined by this method.

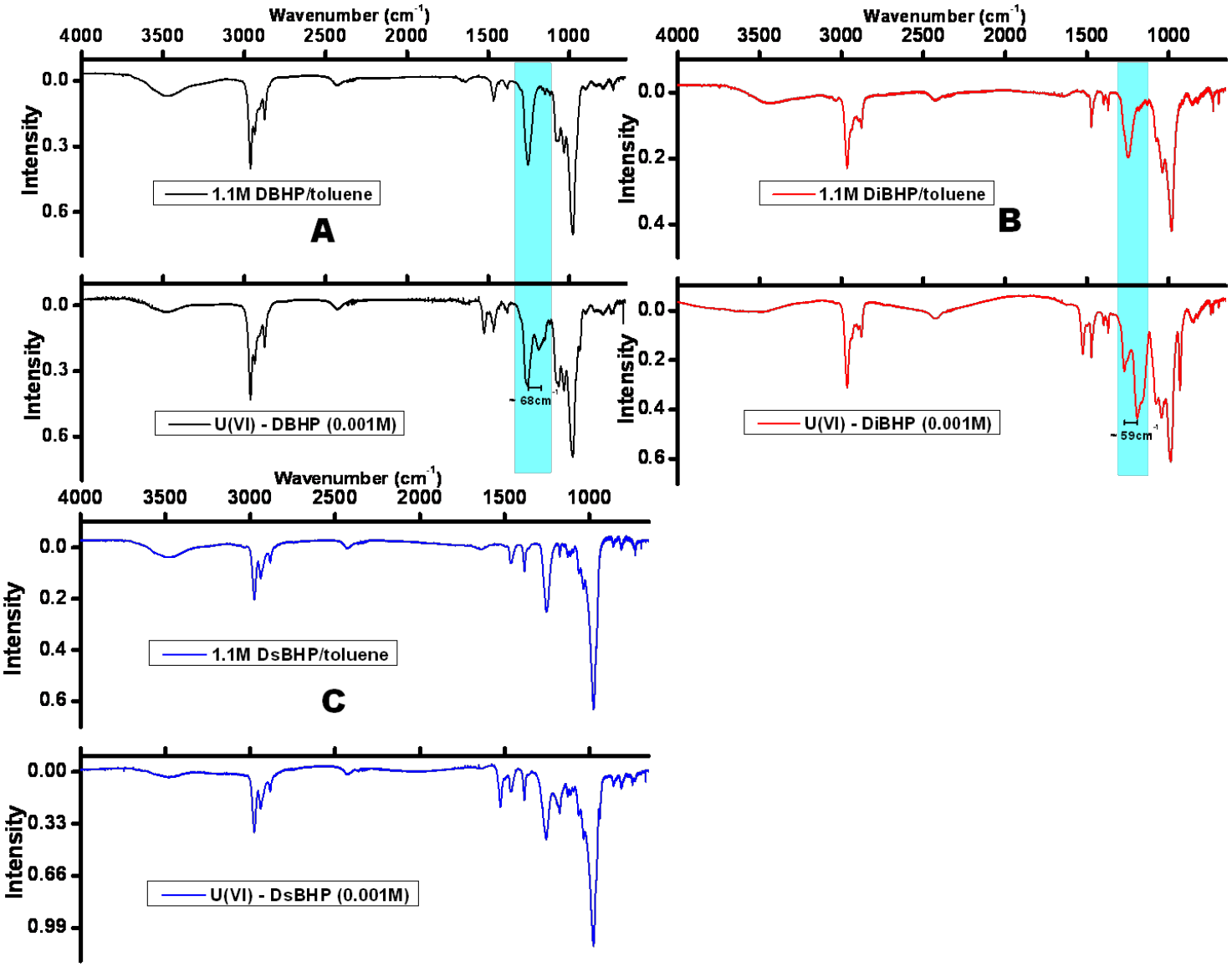


Figure 13S: (A) IR spectrum of DBHP, (B) DsBHP and (C) DiBHP before and after extraction of U(VI) from 0.001M nitric acid.

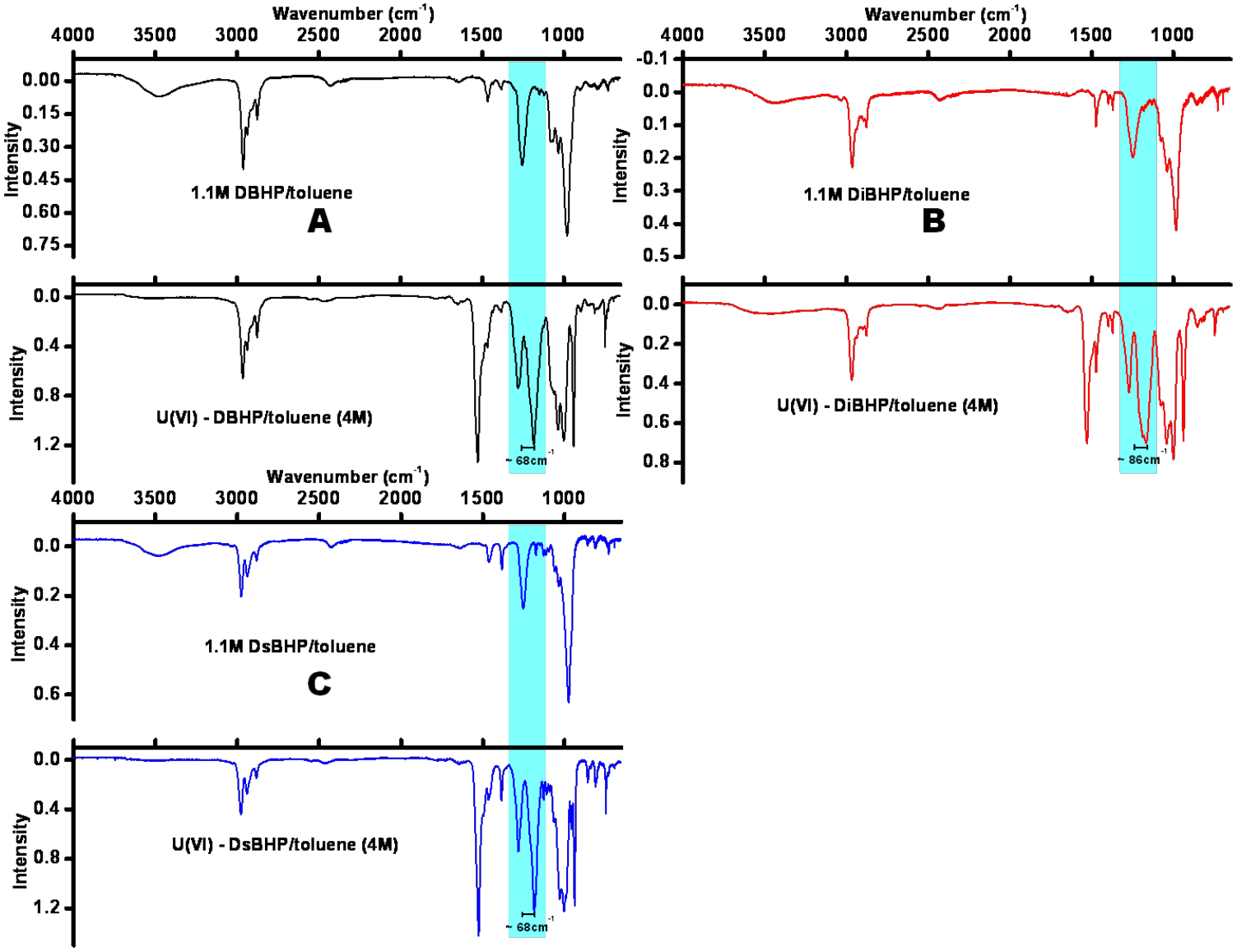


Figure 14S: (A) IR spectrum of 1.1M DBHP/toluene (B) 1.1M DiBHP/toluene and (C) 1.1M DsBHP/toluene before and after extraction of U(VI) from 4M nitric acid.

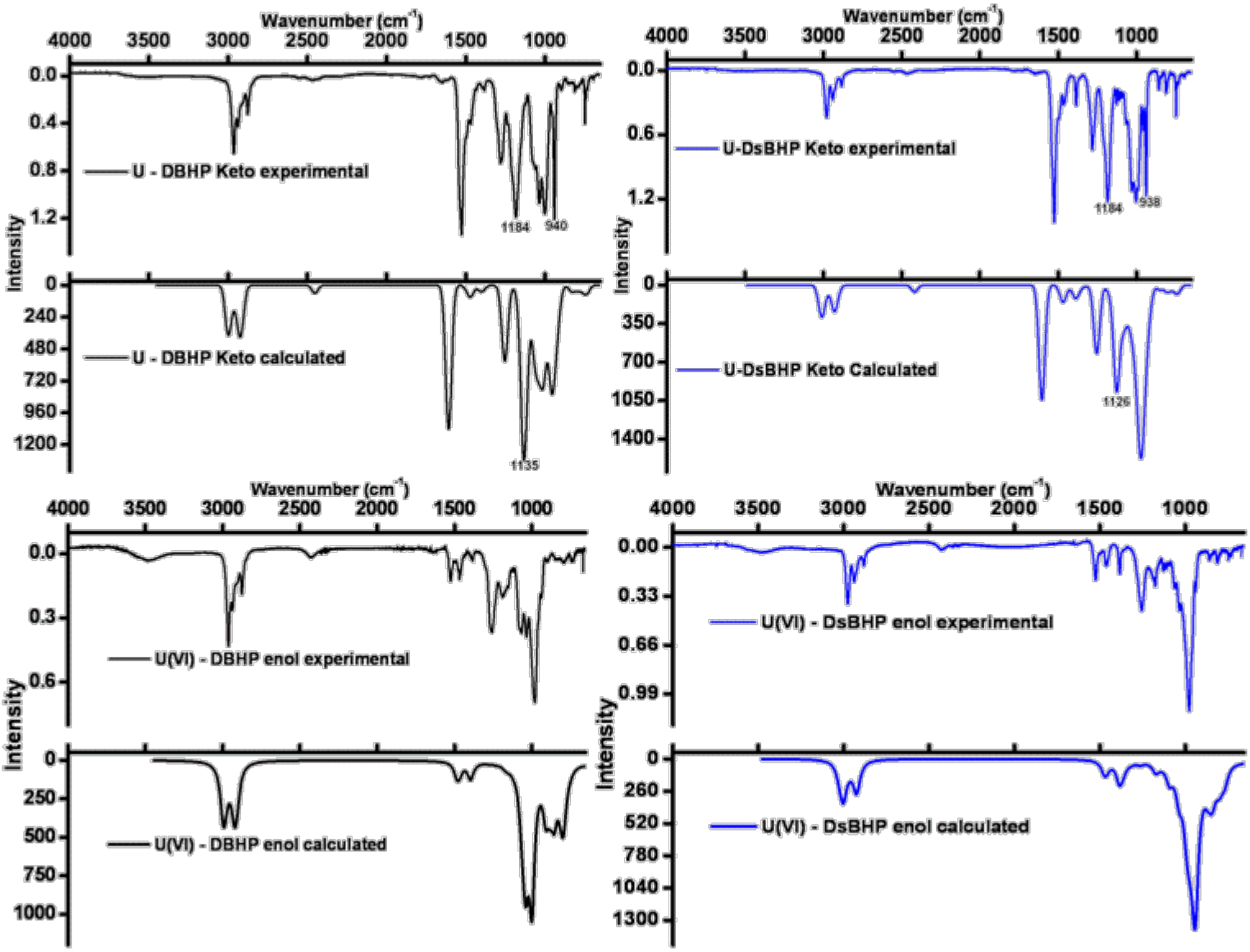


Figure 15S: Comparison of experimental and calculated IR spectra for uranyl nitrate complexes of DBHP and DsBHP both in the keto and enol forms.

Coordinates for the optimized geometries

DBHP keto

P	-1.0090542	0.4318469	0.3823475
O	0.4941436	0.4429780	0.3707824
H	-1.5495297	-0.2378913	1.5245202
O	-1.7911458	-0.2486958	-0.8792332
O	-1.7956908	1.8623601	0.3515046
C	-1.3381495	-1.5676648	-1.3080891
C	-2.2772220	-2.0531555	-2.4000476
H	-1.3524388	-2.2623962	-0.4492136
H	-0.3014322	-1.4912811	-1.6704711
C	-1.9075172	-3.4547127	-2.9050354
H	-3.3072337	-2.0551593	-2.0083863
H	-2.2548648	-1.3332515	-3.2337860
C	-2.8504041	-3.9548670	-4.0043077
H	-0.8714047	-3.4483428	-3.2832862
H	-1.9205193	-4.1640672	-2.0600117
H	-2.5679489	-4.9605872	-4.3469521
H	-3.8895621	-4.0035184	-3.6449755
H	-2.8324620	-3.2865105	-4.8783949
C	-1.3355294	2.8970602	1.2718865
C	-2.2470103	4.1033124	1.1147491
H	-0.2893768	3.1477486	1.0381543
H	-1.3757786	2.5146193	2.3074533
C	-1.8734297	5.2440129	2.0717375
H	-2.1960499	4.4537062	0.0714305
H	-3.2876959	3.7889362	1.2948779
C	-2.7863510	6.4654024	1.9215022
H	-1.9177367	4.8789472	3.1120144
H	-0.8263537	5.5436841	1.8970412
H	-2.5016878	7.2659684	2.6191986
H	-2.7361294	6.8768839	0.9020775
H	-3.8364602	6.2043779	2.1226822

DBHP enol

P	-2.8158604	1.1321394	-0.9101085
O	-2.4356569	2.2107429	0.4342097
O	-2.3524242	-0.3824946	0.0127017
O	-1.6747356	1.2721910	-1.9423949
C	-1.0819288	2.3874311	0.7818744
H	-0.4203367	1.9486825	-0.0091717
H	-0.8491671	3.4872716	0.8178154
C	-1.6330244	-1.3552720	-0.6868463

H	-1.3437256	-0.9722367	-1.7001281
H	-2.2577240	-2.2856007	-0.8393182
C	-0.7687476	1.7656714	2.1530196
C	0.6905479	1.9440815	2.5966588
H	-1.0322852	0.6859021	2.0897735
H	-1.4538166	2.2152653	2.9128096
C	1.0019958	1.3360359	3.9720520
H	1.3631242	1.4869369	1.8317898
H	0.9461875	3.0324118	2.6098691
H	2.0708719	1.4739440	4.2591036
H	0.3767452	1.8008362	4.7697907
H	0.7873883	0.2427714	3.9837998
C	-0.3474233	-1.7699766	0.0535193
C	0.4405865	-2.8845331	-0.6517989
H	-0.6154273	-2.0914154	1.0896032
H	0.2942825	-0.8641433	0.1606000
C	1.7258117	-3.2969684	0.0800374
H	-0.2154806	-3.7803845	-0.7778394
H	0.6956935	-2.5507303	-1.6860393
H	2.2776248	-4.1012197	-0.4607841
H	2.4183070	-2.4311354	0.1924104
H	1.5038246	-3.6726149	1.1059427

DsBHP keto

P	-1.4766486	0.0929190	1.4855052
O	-0.0063587	-0.0449723	1.7503306
H	-2.3200342	0.1218367	2.6364599
O	-2.2314670	-1.0916675	0.6706112
O	-1.9173636	1.4251688	0.6334773
C	-1.5866762	-1.7082661	-0.4918178
C	-2.3238360	-1.2349736	-1.7529680
H	-0.5293760	-1.3579718	-0.5271244
C	-1.6656846	-1.6820854	-3.0655365
H	-3.3783892	-1.5926542	-1.7028643
H	-2.3660272	-0.1241246	-1.7119737
H	-0.6021444	-1.3551932	-3.1183935
H	-1.6848660	-2.7872065	-3.1928480
C	-1.2719384	2.7066851	0.9162383
C	-2.3570779	3.7777063	0.7412099
H	-0.9308955	2.7066845	1.9800117
C	-1.9094146	5.1974298	1.1130253
H	-2.7142657	3.7465289	-0.3141612
H	-3.2249318	3.4780672	1.3710651
H	-1.5202183	5.2433022	2.1556970
H	-1.1102841	5.5761959	0.4384035

H	-2.1925957	-1.2406306	-3.9396075
H	-2.7625176	5.9072693	1.0451963
C	-1.6077213	-3.2159443	-0.2573541
H	-1.0512595	-3.4695723	0.6701030
H	-2.6544949	-3.5772900	-0.1486616
H	-1.1327927	-3.7575054	-1.1041070
C	-0.0522549	2.8637092	0.0102956
H	0.6569434	2.0293562	0.1940277
H	-0.3588629	2.8512379	-1.0596163
H	0.4762451	3.8205389	0.2151063

DsBHP enol

P	-2.8222944	1.0955875	-0.8169475
O	-2.4470128	2.1692603	0.5273497
O	-2.2516836	-0.3959411	0.0868004
O	-1.7217412	1.2995863	-1.8823920
C	-1.0821875	2.4184617	0.8251034
H	-0.4445452	1.9287843	0.0449795
C	-1.6159936	-1.3973258	-0.6688945
H	-1.3137521	-0.9729247	-1.6626029
C	-0.7518798	1.8023832	2.2008995
C	0.7262358	1.8681694	2.6123632
H	-1.0869714	0.7441702	2.1412170
H	-1.3896836	2.2967406	2.9738227
H	1.3783202	1.4168583	1.8283821
H	1.0769004	2.9144153	2.7716866
C	-0.3199797	-1.8301245	0.0540020
C	0.5410725	-2.8623601	-0.6897458
H	-0.5893879	-2.2136969	1.0682057
H	0.2722791	-0.9021304	0.2188992
H	0.0359505	-3.8520865	-0.7725750
H	0.7687758	-2.5192027	-1.7259179
H	0.9126093	1.3103471	3.5598358
H	1.5145609	-3.0326728	-0.1731469
C	-2.5887058	-2.5726667	-0.9020521
H	-2.1456497	-3.3897932	-1.5209646
H	-2.9126105	-3.0033953	0.0746697
H	-3.4995432	-2.2016525	-1.4224388
C	-0.8359521	3.9333879	0.7505727
H	-1.4914753	4.4687126	1.4775519
H	0.2254766	4.2046764	0.9646854
H	-1.0894266	4.2940447	-0.2701276

$UO_2(NO_3)_2 \cdot 2DBHP$

U	0.0159078	-0.0011889	-0.0168240
N	-0.1407391	-0.6399416	2.8831235
O	0.8240344	1.5580998	0.3623677
O	-2.0918673	1.1867263	0.1333202
O	-1.0608322	0.0013779	2.2431853
O	0.8506041	-0.9940852	2.1408033
O	-0.2065679	-0.8817385	4.0701199
N	0.1733765	0.6378558	-2.9165941
O	-0.7922333	-1.5604496	-0.3959920
O	2.1235308	-1.1893702	-0.1666355
O	1.0927423	-0.0041088	-2.2767139
O	-0.8181362	0.9924490	-2.1743004
O	0.2393903	0.8801239	-4.1034987
P	2.5299469	-2.6565824	-0.0813192
H	1.4510600	-3.5504204	0.1373644
P	-2.4983588	2.6538720	0.0480471
O	-3.3058929	3.1597638	1.3501490
H	-1.4202410	3.5474366	-0.1755349
O	-3.4644486	3.0523118	-1.1692308
O	3.3420228	-3.1608171	-1.3811935
O	3.4916753	-3.0560552	1.1390798
C	3.0213969	-2.7361632	-2.7437239
C	4.3127480	-2.6676006	-3.5492869
H	2.5051088	-1.7519233	-2.7184261
H	2.3244459	-3.4931444	-3.1698765
C	4.0647975	-2.2765539	-5.0164684
H	4.9929437	-1.9267132	-3.0692650
H	4.8270262	-3.6553255	-3.4963163
H	3.3624072	-3.0085707	-5.4805618
H	3.5452082	-1.2908683	-5.0518727
C	4.6689640	-2.2615796	1.4674708
C	5.2933675	-2.8406397	2.7294230
H	4.3559035	-1.2049933	1.6168822
H	5.3776869	-2.3060007	0.6101731
C	6.5644066	-2.0860658	3.1539634
H	4.5367170	-2.8095185	3.5460059
H	5.5275594	-3.9153048	2.5514026
H	7.3053761	-2.1102570	2.3201733
H	6.3189034	-1.0100617	3.3152246
C	-2.9804395	2.7368094	2.7120762
C	-4.2684030	2.6743380	3.5235179
H	-2.2790433	3.4922824	3.1336448
H	-2.4675590	1.7508325	2.6863983
C	-4.0152354	2.2855057	4.9903961
H	-4.7795391	3.6636795	3.4707081

H	-4.9533101	1.9347095	3.0482284
H	-3.4991479	1.2979697	5.0255206
H	-3.3080714	3.0159200	5.4497607
C	-4.6435395	2.2583688	-1.4921586
C	-5.2873855	2.8534995	-2.7367325
H	-5.3406414	2.2876499	-0.6247296
H	-4.3285551	1.2052480	-1.6609754
C	-6.5612592	2.1005162	-3.1554396
H	-5.5230713	3.9244800	-2.5393523
H	-4.5418031	2.8377294	-3.5639348
H	-6.3139916	1.0280695	-3.3365793
H	-7.2908242	2.1089285	-2.3113179
C	7.2055190	-2.6604389	4.4242030
H	8.1214180	-2.0952633	4.7048696
H	6.5042580	-2.6150882	5.2874588
H	7.4957667	-3.7263865	4.2850454
C	5.3550183	-2.2118717	-5.8446783
H	5.8736862	-3.1973519	-5.8659662
H	5.1448961	-1.9194059	-6.8969468
H	6.0689217	-1.4671307	-5.4254300
C	-7.2219825	2.6918528	-4.4077035
H	-6.5327331	2.6622310	-5.2812903
H	-8.1397735	2.1277058	-4.6841944
H	-7.5138820	3.7545104	-4.2481905
C	-5.3020426	2.2275638	5.8243991
H	-6.0205349	1.4844318	5.4101397
H	-5.0883719	1.9369750	6.8764752
H	-5.8169569	3.2150150	5.8454133

$UO_2(NO_3)_2$·2DsBHP

U	0.0140666	-0.0014097	-0.0050187
N	0.1724515	-1.7547014	2.3985172
O	0.5629505	1.4027862	0.9732075
O	-2.2557496	0.6023665	0.5623447
O	-0.8845611	-1.0992647	2.0757379
O	1.1555563	-1.5866046	1.5738271
O	0.2525210	-2.4617186	3.3815851
N	-0.1495140	1.7466293	-2.4135973
O	-0.5356852	-1.4058649	-0.9820283
O	2.2813952	-0.6082629	-0.5805620
O	0.9091699	1.0940456	-2.0915279
O	-1.1278336	1.5851845	-1.5819521
O	-0.2356719	2.4450110	-3.4024403
P	2.9578448	-1.9577792	-0.8235824
H	2.0369091	-3.0404984	-0.7924565
P	-2.9310695	1.9536500	0.7984577

O	-3.6806332	2.0911039	2.2182629
H	-2.0083552	3.0342666	0.7518790
O	-4.1011334	2.3244395	-0.2243461
O	3.7145849	-2.0839726	-2.2412288
O	4.1182948	-2.3378508	0.2072089
C	2.9325183	-2.0979553	-3.4947466
C	3.4442671	-3.2966629	-4.3040445
H	1.8580714	-2.2630487	-3.2375538
C	2.6507918	-3.5690141	-5.5891717
H	4.5206504	-3.1269908	-4.5380017
H	3.4045702	-4.1924524	-3.6437579
H	1.5693306	-3.7263794	-5.3751409
H	2.7330188	-2.7352269	-6.3203724
C	4.5206790	-1.5035144	1.3605500
C	4.4086616	-2.3967010	2.6005278
H	3.7923022	-0.6676399	1.4380574
C	4.7709404	-1.6867945	3.9124800
H	3.3575636	-2.7542237	2.6543182
H	5.0559786	-3.2916496	2.4521566
H	5.8420542	-1.3889085	3.9536071
H	4.1560101	-0.7707877	4.0616723
C	-2.8947175	2.1061484	3.4685722
C	-3.3995823	3.3117173	4.2712110
H	-1.8203524	2.2635971	3.2069633
C	-2.6150184	3.5785229	5.5627001
H	-3.3456515	4.2046431	3.6080998
H	-4.4797002	3.1526577	4.4952145
H	-2.7192464	2.7492847	6.2962156
H	-1.5286141	3.7158161	5.3597158
C	-4.4986225	1.4932586	-1.3810859
C	-4.3664583	2.3852776	-2.6201591
H	-3.7766210	0.6510223	-1.4507734
C	-4.7315421	1.6823747	-3.9347765
H	-5.0004282	3.2903426	-2.4741795
H	-3.3094659	2.7260746	-2.6678927
H	-4.1319770	0.7551753	-4.0787430
H	-5.8079329	1.4055719	-3.9840950
H	4.5798577	-2.3572971	4.7784085
H	3.0276607	-4.4865700	-6.0908901
H	-4.5210046	2.3494093	-4.7988838
C	5.9133008	-0.9593184	1.0630071
H	6.6487908	-1.7870365	0.9575364
H	5.9101760	-0.3680425	0.1223162
H	6.2502663	-0.2904647	1.8843724
C	3.0864081	-0.7393673	-4.1685251
H	2.6770181	0.0677966	-3.5255003

H	4.1584934	-0.5331587	-4.3810623
H	2.5264440	-0.7193318	-5.1286548
C	-3.0540041	0.7521498	4.1500620
H	-4.1263870	0.5553846	4.3699444
H	-2.6544779	-0.0608011	3.5078231
H	-2.4889895	0.7344961	5.1073947
C	-5.8979137	0.9600202	-1.0935662
H	-5.9061685	0.3726122	-0.1504467
H	-6.6289336	1.7928847	-0.9967702
H	-6.2328510	0.2887103	-1.9137272
H	-2.9823016	4.5044415	6.0563505

UO_2·2DBHP(enol)

U	0.6168951	0.3852564	0.0286727
O	0.7334939	0.4597712	-1.7676820
O	0.6258644	0.5087582	1.8258947
H	1.2133156	-2.4896267	3.0510916
C	2.1486411	-2.8806586	2.5834523
O	1.8641805	-3.3738908	1.2573299
H	2.8744525	-2.0384426	2.5192706
C	2.7260920	-4.0321728	3.4010775
P	1.3663235	-2.3326444	0.0848907
C	3.1004889	-3.6177446	4.8334970
H	3.6239898	-4.4232784	2.8695186
H	1.9854552	-4.8646575	3.4229570
O	1.7050474	-3.3533495	-1.1616625
O	2.3741325	-1.0774566	0.0698297
C	3.7083771	-4.7649757	5.6513293
H	3.8216433	-2.7674146	4.7955378
H	2.1960695	-3.2266618	5.3566027
C	1.2144216	-3.0248707	-2.4794808
H	3.9694663	-4.4342025	6.6808366
H	2.9998543	-5.6192822	5.7407625
H	4.6377078	-5.1523063	5.1757222
H	1.8961005	-2.2761731	-2.9440844
H	0.2038219	-2.5547653	-2.4066089
C	1.1542397	-4.2990095	-3.3160743
C	0.6482487	-4.0394477	-4.7448136
H	0.4931354	-5.0335697	-2.8010777
H	2.1706250	-4.7552974	-3.3453510
C	0.5904223	-5.3068270	-5.6074230
H	-0.3657026	-3.5762106	-4.6988457
H	1.3047816	-3.2845023	-5.2383908
H	0.2145413	-5.0820825	-6.6300294
H	1.5965159	-5.7720559	-5.7124434

H	-0.0848284	-6.0710209	-5.1603688
H	-2.3019599	2.4671217	-5.4946845
C	-1.8805734	3.4552667	-5.1937772
C	-2.2745506	3.7527254	-3.7373775
C	-2.3481482	4.5316386	-6.1820308
H	-0.7723438	3.3459800	-5.2629525
C	-1.7759948	2.6842156	-2.7690295
H	-1.8665267	4.7408264	-3.4220651
H	-3.3829515	3.8262943	-3.6469980
H	-2.0517980	4.2787783	-7.2240648
H	-3.4556381	4.6452080	-6.1644237
H	-1.9077695	5.5248521	-5.9381576
O	-2.2473476	2.9958517	-1.4416933
H	-2.1584109	1.6777299	-3.0568165
H	-0.6612940	2.6287705	-2.7826971
P	-1.4034589	2.4298027	-0.1443578
O	-2.4128224	3.1065985	0.9677394
O	-1.5868792	0.8202380	-0.0666602
C	-2.2413119	2.7729224	2.3599980
H	-2.6246820	1.7415510	2.5369288
H	-1.1573048	2.7755563	2.6291202
C	-3.0100059	3.7908371	3.1970711
C	-2.9678067	3.4783068	4.7017233
H	-4.0658032	3.8130120	2.8408885
H	-2.5911207	4.8051000	3.0020759
C	-3.7274427	4.5047304	5.5524032
H	-3.3928331	2.4622506	4.8789317
H	-1.9064899	3.4273336	5.0419921
H	-3.6871362	4.2436211	6.6329913
H	-3.2979224	5.5254330	5.4358018
H	-4.8000186	4.5598772	5.2584772

UO_2·2DsBHP(enol)

U	0.5946599	0.4467130	-0.1309553
O	0.6242795	0.5469961	-1.9322246
O	0.6361270	0.5645999	1.6689703
H	1.7721299	-1.7809052	2.5128897
C	2.6003791	-2.5223125	2.4037802
O	2.6943485	-2.9266591	1.0045078
C	2.2436482	-3.7893492	3.1943154
P	1.9879068	-2.0139634	-0.1652537
C	2.0047987	-3.5576019	4.6921478
H	3.0564583	-4.5363227	3.0400299
H	1.3294183	-4.2235878	2.7303700
O	2.6075333	-2.8811392	-1.4151282
O	2.6498693	-0.5424499	-0.1437570

H	2.9223639	-3.2093236	5.2156118
H	1.2084847	-2.7984953	4.8657329
C	1.9914459	-2.8155209	-2.7365661
H	1.1582633	-2.0725723	-2.7121590
C	1.4157879	-4.2065171	-3.0418916
C	0.6684674	-4.3076360	-4.3783731
H	0.7273533	-4.4723202	-2.2075628
H	2.2497895	-4.9448063	-3.0040021
H	-0.1469637	-3.5520995	-4.4483712
H	1.3435554	-4.1577271	-5.2495516
H	-2.5528413	3.3205047	-5.5216611
C	-2.0086672	3.9528518	-4.7859402
C	-2.5507516	3.7811897	-3.3605857
H	-0.9288087	3.6862711	-4.8459416
C	-2.3454077	2.3787647	-2.7689690
H	-2.0495455	4.5058698	-2.6793240
H	-3.6384468	4.0219117	-3.3244271
O	-2.8296330	2.4187112	-1.3935798
H	-1.2544122	2.1424391	-2.7642972
P	-1.8181206	2.0170366	-0.1597936
O	-2.8807415	2.4464227	1.0199914
O	-1.6526819	0.3999233	-0.1324313
C	-2.5016296	2.3197568	2.4227806
H	-1.4133044	2.0779340	2.4861394
C	-2.7495756	3.6889562	3.0731146
C	-2.3347250	3.7780499	4.5477552
H	-3.8292067	3.9401295	2.9561057
H	-2.1887490	4.4455987	2.4788728
H	-2.9423069	3.1090690	5.1962459
H	-1.2644172	3.5035029	4.6883099
C	3.9181823	-1.8615506	2.8055033
H	4.7621711	-2.5775222	2.6911100
H	4.1139442	-0.9795924	2.1599497
H	3.8842753	-1.5182425	3.8626139
C	-3.3017855	1.1658889	3.0251199
H	-3.0931290	0.2267624	2.4703417
H	-3.0294199	1.0068897	4.0914584
H	-4.3928521	1.3755343	2.9643024
C	3.0584443	-2.3286545	-3.7142410
H	2.6401599	-2.2288968	-4.7394482
H	3.4413817	-1.3349174	-3.3990200
H	3.9127489	-3.0407204	-3.7468969
C	-3.0887029	1.2575754	-3.4928751
H	-2.7369196	1.1613594	-4.5432473
H	-2.9121897	0.2893277	-2.9782388
H	-4.1833605	1.4566422	-3.5009928

H	1.6810523	-4.4995585	5.1866214
H	-2.4657052	4.8144028	4.9290976
H	-2.1105083	5.0085716	-5.1200143
H	0.2029042	-5.3111059	-4.4913779

$Am(NO_3)_3 \cdot 3DBHP$

Am	-0.08929320	0.11379520	-0.06159110
O	1.51510610	-0.11878300	-1.93723090
O	0.05152980	1.48277370	-2.14373990
O	1.45814300	1.07136540	-3.78670560
O	-1.89078430	-1.40786410	0.81278380
O	-3.00296150	-1.00660650	2.66831450
O	1.34877100	-1.54347480	1.07809130
O	3.21672910	-1.00811000	2.11184120
N	1.03223950	0.82506810	-2.68074900
N	-2.15499440	-0.70341460	1.85926510
N	2.23669280	-0.69310480	1.47750920
O	-1.43461020	0.37465390	1.97607000
O	1.98988250	0.54055620	1.14179570
C	2.58545249	4.19726519	0.94510270
O	1.55895021	4.44125701	1.91032862
C	3.87103427	4.85951450	1.36807372
H	2.24337447	4.59382850	-0.04142909
H	2.72364303	3.09309060	0.84883440
P	0.02746222	3.81507409	1.31029572
C	4.97892038	4.61851795	0.36435004
H	3.70644296	5.96351003	1.48344876
H	4.19451857	4.44766919	2.36052479
O	0.02255083	2.43304705	0.86499499
H	-0.28778403	4.69765812	0.43793713
O	-1.06289519	4.21802388	2.63179191
C	6.26448600	5.28083786	0.78731666
H	5.14351685	3.51455052	0.24898303
H	4.66465030	5.01102147	-0.63881111
C	-2.38425631	3.77412671	2.31263662
H	7.06624495	5.09029747	0.03377449
H	6.12613794	6.38498520	0.88366466
H	6.60630880	4.88439275	1.77400450
C	-3.35361335	4.19964227	3.38477587
H	-2.36840030	2.66167131	2.21406489
H	-2.67308585	4.20826608	1.32487843
C	-4.76378506	3.74351671	3.07442538
H	-3.03355269	3.77480984	4.37284795
H	-3.35186486	5.31875682	3.46722183
C	-5.73312053	4.16899345	4.14662201
H	-5.08384444	4.16834523	2.08638270

H	-4.78008088	2.62610459	2.97302715
H	-6.76505258	3.82257581	3.89750370
H	-5.44411973	3.73489153	5.13434592
H	-5.74867097	5.28146215	4.24529328
O	-2.26099428	0.67052220	-1.16783224
P	-3.41355030	1.04295677	-1.96859608
H	-4.47768975	1.35437753	-1.32830817
O	-4.01720803	-0.17276648	-3.08895956
O	-3.21715591	2.43501991	-3.02745842
C	-4.23932079	-1.39933747	-2.38818177
C	-2.72282173	3.54372246	-2.27160633
C	-4.89999382	-2.40751130	-3.29222591
H	-4.88106697	-1.18637580	-1.49917447
H	-3.25455606	-1.78107666	-2.02475452
C	-2.64426937	4.77479943	-3.13675265
H	-1.71428488	3.27691709	-1.87261619
H	-3.40746328	3.71329366	-1.40553629
C	-5.14842899	-3.71906894	-2.57734919
H	-5.87483564	-1.99671439	-3.66657489
H	-4.23947986	-2.60467437	-4.17770082
C	-2.12348560	5.96773824	-2.36303859
H	-1.97252461	4.57733121	-4.01366378
H	-3.66663856	5.02291527	-3.52715956
C	-5.80916737	-4.72721345	-3.48140494
H	-4.17361163	-4.12986332	-2.20301684
H	-5.79552286	-3.53690066	-1.67888315
C	-2.04488139	7.19879794	-3.22823263
H	-2.79521743	6.16521030	-1.48615389
H	-1.10680948	5.73011601	-1.95186669
H	-5.98256572	-5.68516007	-2.93439475
H	-6.79385938	-4.34531322	-3.84485827
H	-5.16744685	-4.93987495	-4.37052491
H	-1.65901705	8.06472966	-2.63813109
H	-1.36030939	7.02906374	-4.09432498
H	-3.05344056	7.46533342	-3.62739634
H	-0.37871638	-6.80549303	0.55662101
C	-0.67403936	-5.86721236	1.09665017
C	-0.23582426	-4.66848142	0.29589379
C	-0.03698455	-5.88336148	2.47027769
H	-1.79102104	-5.86127577	1.20400258
O	-0.85201550	-4.67970134	-0.99448696
H	-0.52137345	-3.72155489	0.81485103
H	0.87249721	-4.67039622	0.15738169
C	-0.47527026	-7.08207958	3.27104475
H	1.07996979	-5.88930801	2.36293119
H	-0.30991949	-4.94314408	3.01859762

P	-0.23366856	-3.33900048	-1.95248919
H	0.00592025	-7.07357742	4.27868172
H	-1.58361235	-7.08011518	3.40938649
H	-0.18991534	-8.02894864	2.75183766
O	-0.29836641	-2.02295447	-1.34244598
H	0.93123595	-3.76499347	-2.27009227
O	-1.11146428	-3.54802167	-3.46357649
C	-0.72760951	-2.52338224	-4.38426620
C	-1.34930945	-2.77160318	-5.73410867
H	0.38681103	-2.51549076	-4.45862612
H	-1.05727428	-1.53851534	-3.97326246
C	-0.96078349	-1.70124436	-6.73227287
H	-1.02666050	-3.77499071	-6.11923067
H	-2.46709014	-2.77686247	-5.63533391
C	-1.58245048	-1.94952614	-8.08213718
H	-1.28343208	-0.69788124	-6.34716776
H	0.15658783	-1.67203672	-6.83119319
H	-1.28293698	-1.14941194	-8.80120449
H	-1.25280632	-2.93446664	-8.49297949
H	-2.69687449	-1.95768000	-8.00759124

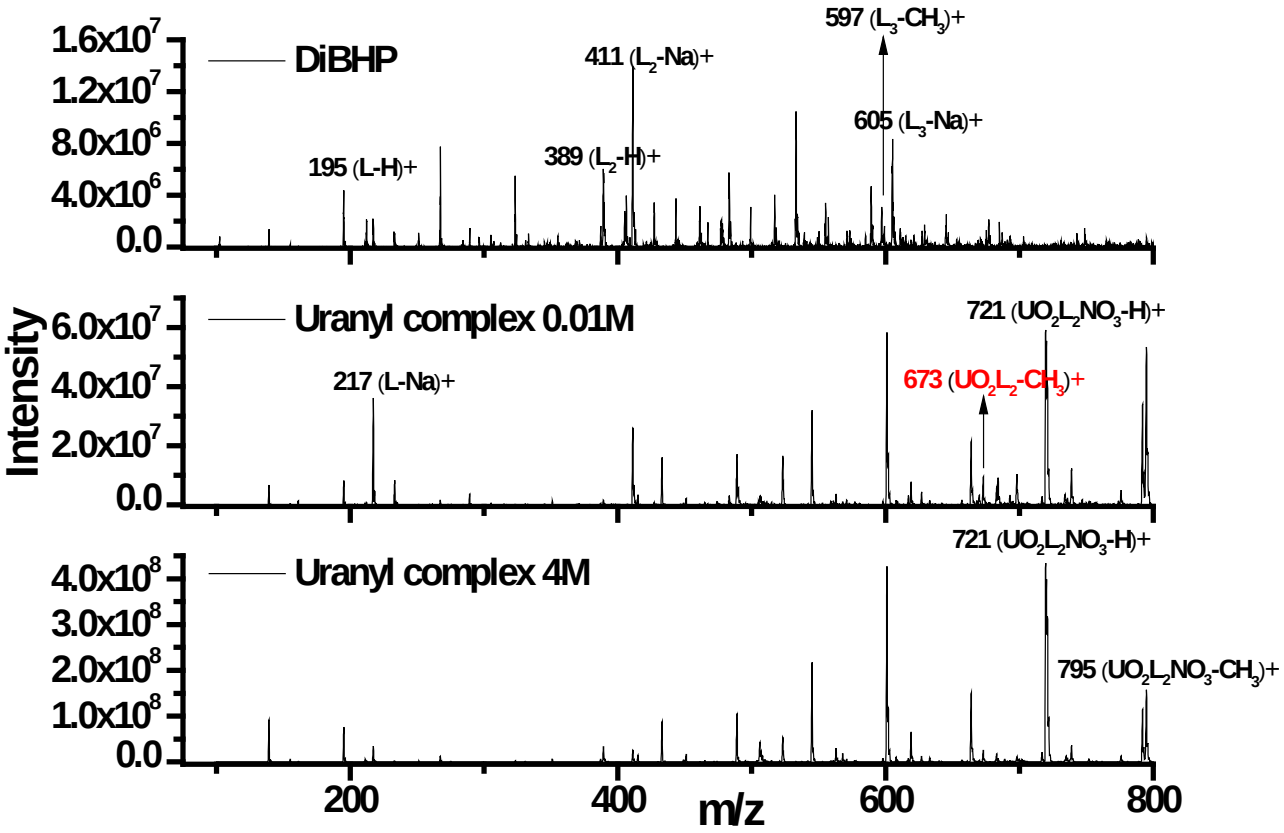


Figure 16S: ESI mass spectra for the bare ligand DiBHP compared with the organic phase uranyl complexes extracted from 0.01M and 4M nitric acid.